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in CdS Single Crystals**

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X-RAY DAMAGE AND ANNEALING OF THESE DEFECTS
IN CdS SINGLE CRYSTALS⁺

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ABSTRACT

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The influence of x-ray damage at 250 keV and 300 keV in ultra-high vacuo on the spectral distribution of photoconductivity and conductivity glow curves is described. The observed damage can be explained by assuming a production of sulfur vacancies by x-rays and a later diffusion determined formation of associates of these vacancies with acceptors resulting in recombination centers. The threshold energy for sulfur vacancy formation lies at about 250 keV.

X-ray damage can be used as a tool to produce intrinsic defects in CdS single crystals; this facilitates the analysis of their electrical and optical properties. Damage as a function of the x-ray energy is used to distinguish between defects in the heavy or light sublattices of binary compounds. All these investigations are usually based on the assumption that predominantly single defects, such as vacancies or interstitials are produced, and spatial inhomogeneities, e.g. surface effects, can be neglected.

⁺The work is supported in part by the National Aeronautics and Space Administration and by the Office of Naval Research.

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These assumptions, however, were rarely justified. Previous x-ray damage of CdS crystals was performed in vacua of approximately 10^{-6} torr. It has been observed¹⁻⁴ that x-rays of about 100 keV already produce major changes in electrical properties of these crystals, as seen in thermally stimulated current (TSC) curves (conductivity glowcurves), and the spectral distribution of the photoconductivity.

Here results of x-ray damage investigations in ultra-high vacua (10^{-10} torr range^{*}) are reported which indicate that earlier results were influenced by surface effects caused by ionization of the ambient atmosphere.

Undoped high insulating CdS single crystals were used with four evaporated Au-Cr electrodes, the two inner electrodes were connected to high impedance electrometers for potential probing in order to eliminate barrier layer effects at the current electrodes.

The spectral distribution of the photocurrent was measured at about 2×10^{14} photons/cm² with a wavelength sweep rate of about 200 Å/hr., in order to achieve steady state photocurrents for each wavelength. The TSC curves were measured after irradiation at 490 mμ, and steady state currents were achieved at -180°C with a heating rate of about 0.4 deg./sec.

The x-ray irradiation was conducted at room temperature from a polychromatic source⁺ at 100, 150, 200, 250, and 300 keV; the reported 300 keV irradiation for 2 hours at 7.5 ma and 45 cm source-crystal distance (unfiltered).

* The crystal was held in the 10^{-10} torr range during the entire reported program (several months).

+ The authors are indebted to Frankford Arsenal, Philadelphia for the use of the x-ray source.

In contrast to earlier investigations at higher pressures of the ambient atmosphere, irradiations below 250 keV result in very small changes in electrical properties, indicating that a threshold for production of electrically active defects lies at about 250 keV.

In order to obtain further information on x-ray produced defects, the crystal was then annealed at temperatures between 100° and 300°C for one hour and consequently cooled to room temperature at a rate of about one degree per minute. After a final annealing at 300°C^{**} all following x-ray damage and annealing cycles were essentially reproducible.

Figure 1 shows a family of TSC curves: (1) before and (2) directly after x-ray damage at 250 keV. A slight decrease of 150°K peak and an increase of 300° peak is observed. Waiting at room temperature (in the dark) reduces both peaks (curves (3) and (4)), annealing at 100°C essentially reproduces the original TSC curve before damage. (The slight shift towards higher currents is characteristic for heat treatments in vacuo and independent of x-ray damage.)

Figure 2 shows a similar but enhanced influence of x-ray damage of 300 keV on TSC curves, while Figure 3 indicates that annealing at 100°C is insufficient but 150°C is sufficient to restore the original state before damage.

A similar behavior is shown for spectral distributions of the photoconductivity in Figures 4 and 5: after x-ray damage the photoconductivity decreases, while after annealing at 100°C a slight increase and after annealing of 150°C an essentially complete return to the original curve is observed (also here a slight increase over the value of the original curve indicates the influence of the heat treatment in vacuo).

**** Probably causing the desorption of a disturbing surface layer.**

Disregarding some changes in the shape of the spectral distribution curve of the photocurrent, the effect of x-ray damage can essentially be described as a parallel shift towards lower currents indicating a wavelength independent reduction of the photoelectric gain factor. An increase of the density of recombination centers as a result of the damage is a possible explanation. The further decrease of the spectral distribution curve after waiting at room temperature indicates an increase of the density of these recombination centers.

The TSC curves show beside a shift to lower values, which can be similarly understood, an increase of the 300° peak directly after x-ray damage, indicating an electron trap at about 0.5 eV. After waiting at room temperature the density of the trap decreases, while the density of recombination centers increases, as it can be concluded from the stronger decrease of the 300° K peak on top of a parallel shift of the TSC curves.

This indicates that x-ray damage near the threshold of about 250 keV produces electron traps at about 0.5 eV. After waiting at room temperature these defects probably associate with others to form recombination centers.*

The fact that this formation of recombination centers is possible at room temperatures in undoped CdS single crystals is well known from photochemical reactions.**

* Recombination centers are very probably associates of donors and acceptors.

**The CdS crystal used for the reported investigations shows photoelectrical reactions already at room temperatures in agreement with observations by Borhardt.⁵

At temperatures of 100° to 150°C the recombination centers dissociate, allowing the x-ray produced centers to recombine.

To give a microscopic model is more difficult. However, since the damage and annealing cycle of the undoped crystal is well reproducible in ultra-high vacua, one may attempt a description using simple defects of the intrinsic lattice. It is most probable that x-ray damage at the lower threshold produces disorder in the sulfur sublattice. Here the simple defect produced by x-rays is the displacement of a sulfur atom, creating a sulfur vacancy and an adjacent sulfur interstitial. If this takes place in the neighborhood of other crystal defects, e.g. low angle boundaries, dislocations, etc., which may act as creation centers* for x-ray produced defects, the "sulfur interstitial" can associate with these defects, resulting in a more or less isolated sulfur vacancy.

This sulfur vacancy acts as an electron trap and produces the 300°K peak in the TSC curve in agreement with a model proposed by Bube.⁶ The transformation of this electron trap into a recombination center is not yet understood. However, in the neighborhood of crystal defects, where diffusion is enhanced, it is not difficult to assume a migration of oppositely charged defects in order to form associates already at room temperature, especially since a migration over a few lattice constants only is necessary, although the diffusion of sulfur vacancies over a microscopic distance through the lattice is observed at considerably higher temperatures only.⁷

It therefore shall be proposed that x-ray damage in undoped CdS near the 250 keV threshold produces sulfur vacancies in the neighborhood of crystal defects, which in turn can associate to recombination centers with acceptors already at room temperature. These defects anneal essentially at temperatures between 100° and 150°C .

* Energy transfer from the position of x-ray absorption to the creation center by lattice impacts.

LITERATURE

1. K. W. Böer, E. H. Weber, and B. Wojtowicz, Z. Phys. 168, 115 (1962).
2. B. A. Kulp, J. Appl. Phys. 32, 1966 (1961).
3. E. H. Weber and B. Wojtowicz, Phys. Stat. Sol. 1, K7 (1961).
4. T. Y. Sera, V. V. Serdyuk, and J. M. Sherchenko, Fiz. Tver. Tela. 3, 3537 (1961).
5. W. Borchardt, Phys. Stat. Sol. 2, 1575 (1962).
6. R. H. Bube and L. A. Barton, RCA Review 20, 564 (1959).
7. H. H. Woodbury, Phys. Rev. 134, A 492 (1964).

FIGURE CAPTIONS

- Fig. 1 TSC curves of undoped CdS single crystal before and after damage with 250 keV x-rays and after annealing at 100°C.
- Fig. 2 TSC curves of undoped CdS single crystal before and after damage with 300 keV x-rays.
- Fig. 3 TSC curves of undoped CdS single crystal after x-ray damage as given for Fig. 2 and after annealing at 100°C and 150°C.
- Fig. 4 Spectral distribution of photoconductance of undoped CdS single crystal before and after x-ray damage at 300 keV (measured at -190°C).
- Fig. 5 Spectral distribution of photoconductance of undoped CdS single crystal after x-ray damage (300 keV) and after annealing at 100°C and 150°C (measured at -190°C).

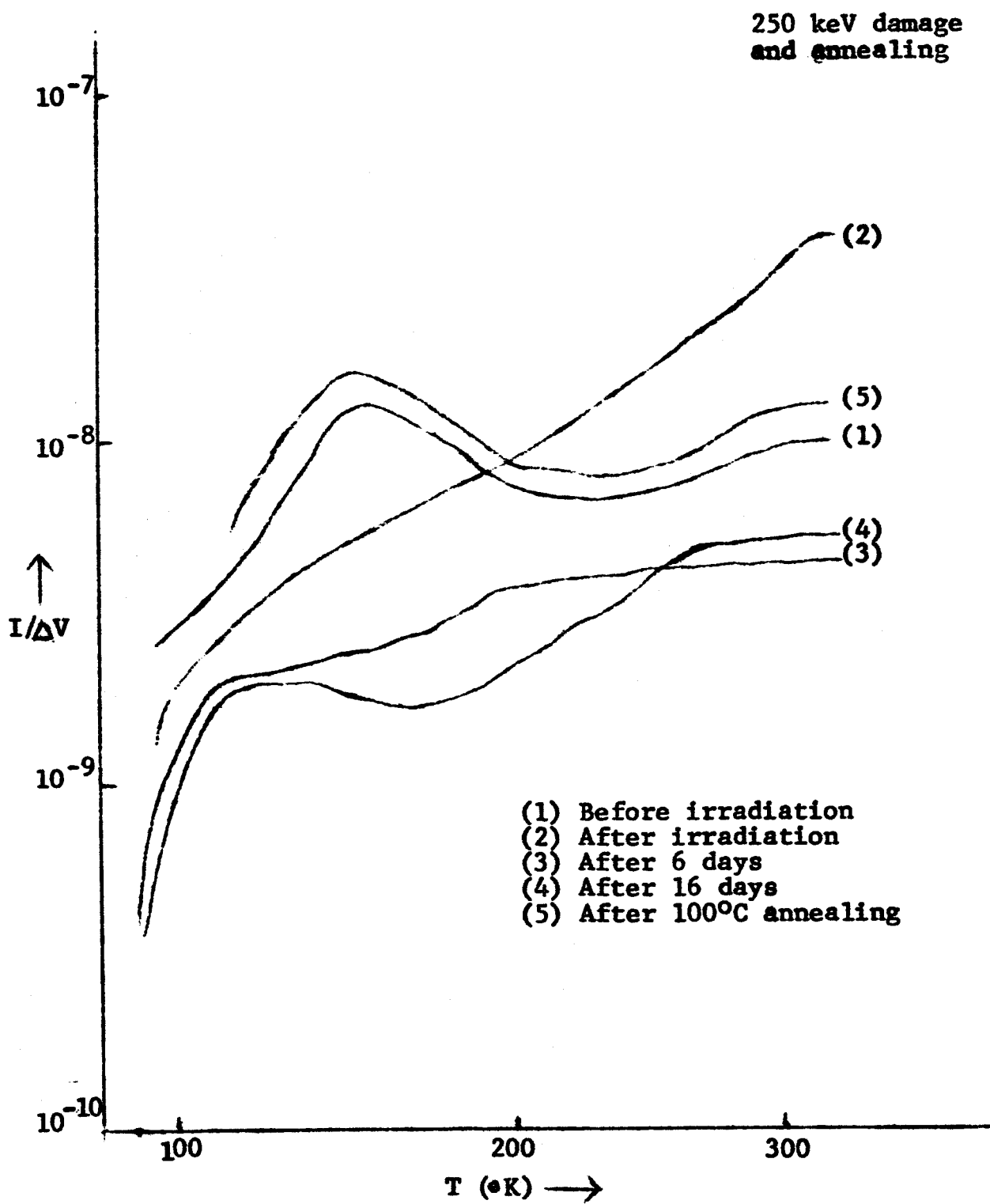


Figure 1

TSC curves of undoped CdS single crystal before and after damage with 250 keV x-rays and after annealing

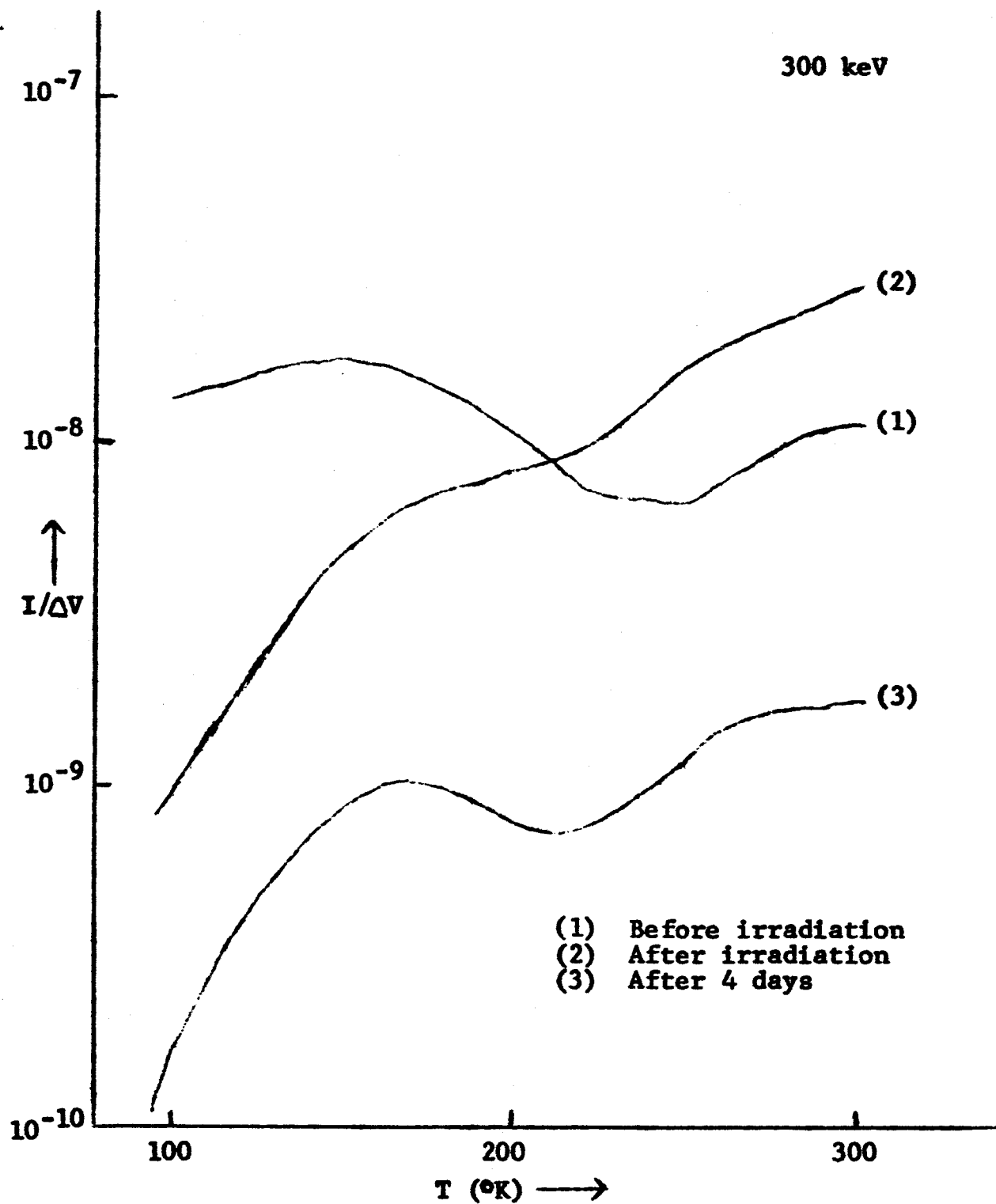


Figure 2

TSC curves of undoped CdS single crystal before and after damage with 300 keV x-rays.

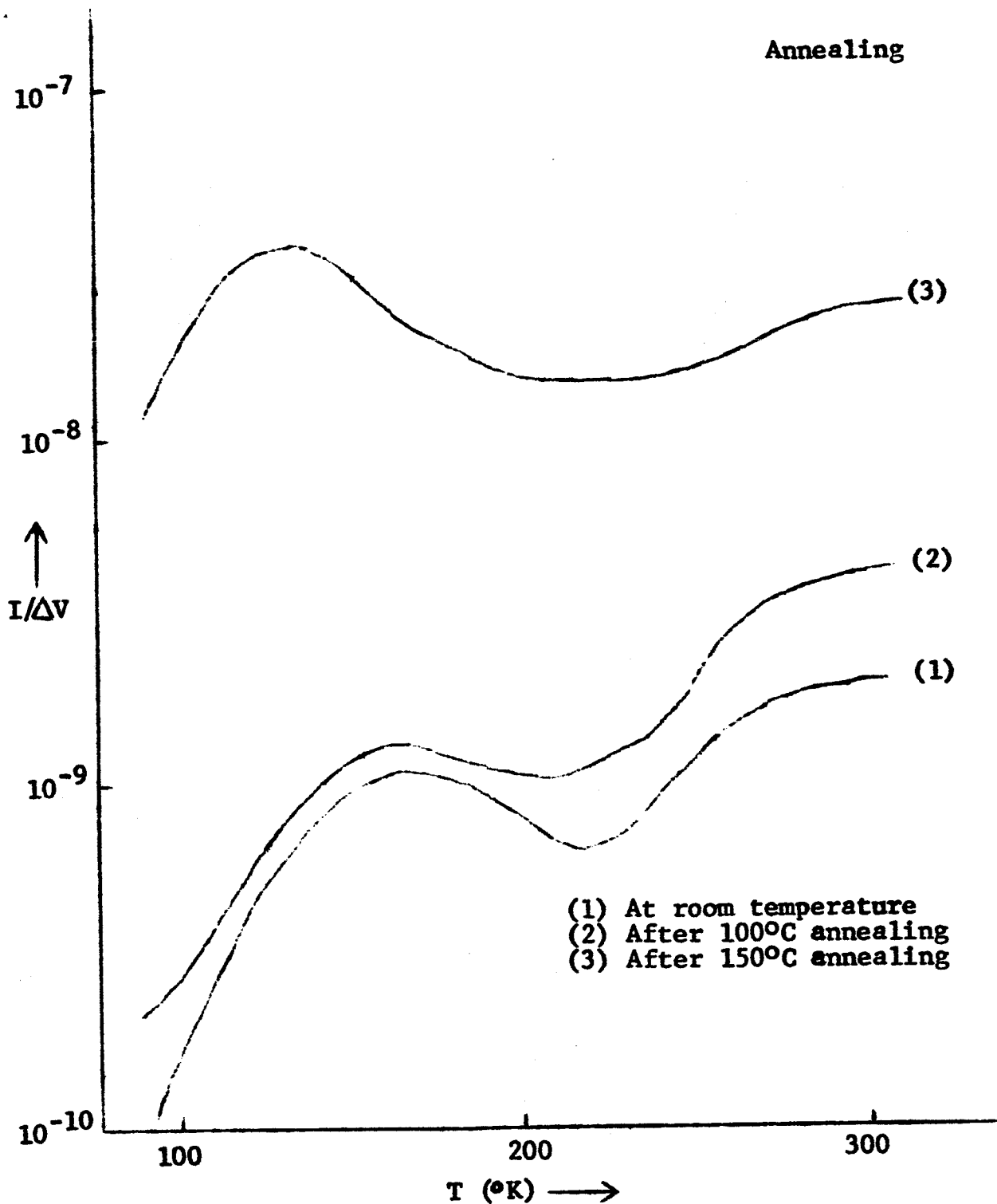


Figure 3

TSC curves of undoped CdS single crystal after x-ray damage as given for Fig. 2 and after annealing at 100°C and 150°C.

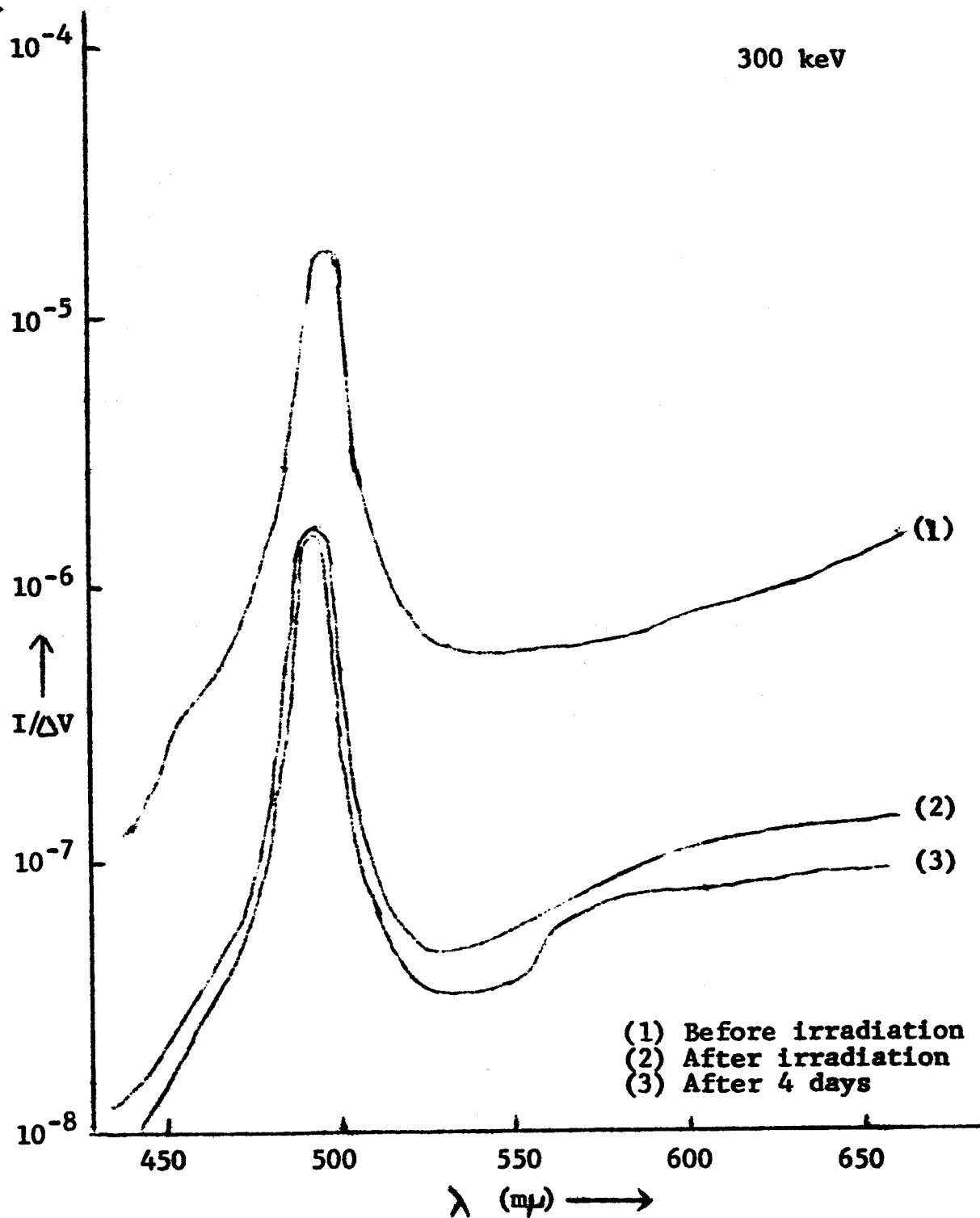


Figure 4

Spectral distribution of photoconductance of undoped CdS single crystal before and after x-ray damage at 300 keV (measured at room temperature).

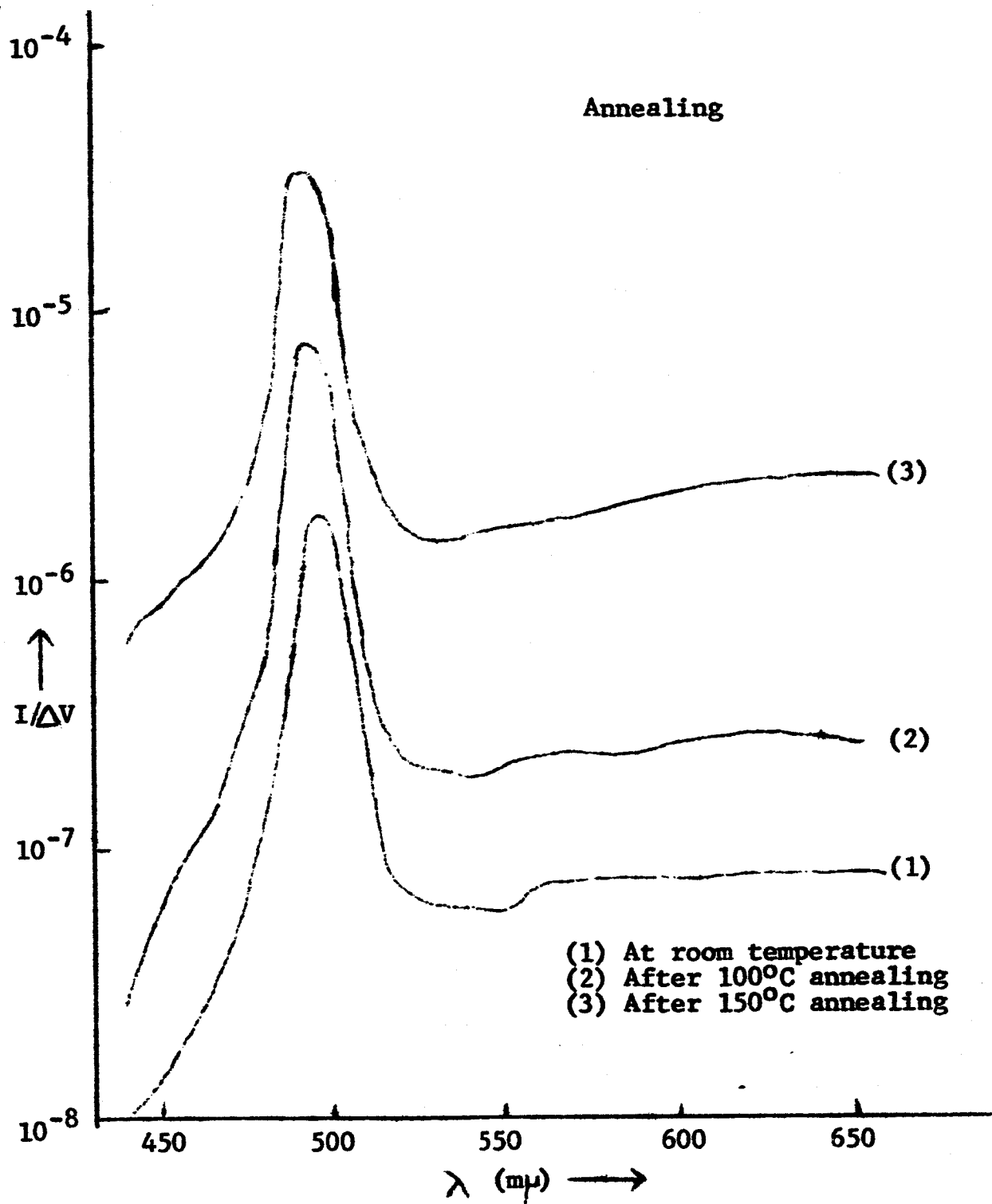


Figure 5

Spectral distribution of photoconductance of undoped CdS single crystal after x-ray damage (300 keV) and after annealing at 100° and 150°C (measured at room